

VOLTAMMETRIC REDOX WAVE AT A STATIONARY ELECTRODE, I.
Farsang Gyorgy, Rozsondai Bela and Tomcsanyi Laszlo

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VOLTAMMETRIC REDOX WAVE AT A STATIONARY ELECTRODE, I.

Theoretical current-potential curves.

Farsang Gyorgy, Rozsondai Bela and Tomcsanyi Laszlo
Hungarian Academy of Science Chemical-Structural Research
Laboratory, Budapest
Metallurgy Research Institute, Budapest

In a solution containing both the oxidized and reduced /233* forms of a polarographically reversible redox system, with a dropping mercury working electrode, the polarization curve in the well known redox wave described by Heyrovsky [1]. In addition to its theoretical significance this phenomenon is useful for the concentration measurement of both components in a reversible redox system, if these concentrations are the same order of magnitude.

In our previous article we presented a special cyclical voltammetric technique [2,3], in which we get the reproducible redox wave of a reversible redox system at a stationary electrode.

The purpose of our present work is the determination and examination of the theoretical current-potential equation of the cyclical voltammetric redox wave. We used the Nicholson and Shain [4] method of calculation.

The cyclical voltammetric redox wave cannot be characterized with the numerous available current-potential equations in the case of voltammetric measurements with stationary working electrodes. The condition, that both components of the reversible redox system be present in simultaneously measurable quantities, was not stipulated in any of the theoretical derivations in the literature.

The current-potential equation.

We assume that during the voltammetric redox wave a reversible electrode reaction takes place on the plane surface

*Numbers in the margin indicate pagination in the foreign text. 1

stationary electrode.



The stationary solution contains both the oxidized and reduced forms of the redox system, and in addition the usual concentrations of the supporting electrolyte for the prevention of mass transport by migration. Let's assume furthermore that mass (and charge) flows only at right angles to the electrode surface. The electrode potential (E) is changed in time (t):

$$E = E_i - vt \quad (2)$$

E_i is the starting potential, v is the speed of polarization (for the cathode process $v > 0$).

The current (i) is a function of time, and thus, a function of the potential:

$$i = nFAf(t) \quad (3)$$

F is the Faraday number, A is the surface of the plane electrode, $f(t)$ is the flow flux of the oxidized or reduced material on the electrode surface.

Under the above circumstances mass transport takes place only via diffusion:

$$f(t) = + D_{\text{ox}} \left. \frac{\partial C_{\text{ox}}}{\partial x} \right|_{x=0} \quad (4)$$

x is the distance measured from the electrode surface; $C_{\text{ox}}(x,t)$ is the concentration of the oxidized form in the solution at place x , and time t ; D_{ox} is the diffusion constant for the oxidized form (we consider it independent of the concentration). In equation (4) the sign agrees with polarographic conventions.

The diffusion problem is described by the following parametric equations.

$$\begin{aligned}\frac{\partial C_{ox}}{\partial t} &= D_{ox} \frac{\partial^2 C_{ox}}{\partial x^2} \\ \frac{\partial C_{red}}{\partial t} &= D_{red} \frac{\partial^2 C_{red}}{\partial x^2}\end{aligned}\quad (5)$$

The differential equations are to be solved with the following stipulations:

$$\begin{aligned}x \geq 0, t = 0: \\ C_{ox} &= C_{ox}^* > 0 \\ C_{red} &= C_{red}^* > 0\end{aligned}\quad (6)$$

$$\begin{aligned}x \rightarrow \infty, t \geq 0: \\ C_{ox} &\rightarrow C_{ox}^* \\ C_{red} &\rightarrow C_{red}^*\end{aligned}\quad (7)$$

$$\begin{aligned}x = 0, t \geq 0: \\ -D_{ox} \frac{\partial C_{ox}}{\partial x} - D_{red} \frac{\partial C_{red}}{\partial x} = 0\end{aligned}\quad (8)$$

$$\frac{C_{ox}}{C_{red}} = \exp \left[\frac{nF}{RT} (E - E^0) \right]\quad (9)$$

where C_{red} and D_{red} are the concentration and diffusion constant of the reduced form, C_{ox}^* and C_{red}^* are the starting concentrations, R the universal gas constant, T the temperature and E^0 the standard potential of the redox system.

The condition expressed in (6) is that both components of the redox system are present in the solution in homogeneous concentration distribution at the beginning of the measurement. (Before starting a new measurement the solution has to be homogenized by stirring.)

According to condition (7) during the time of the measurement (t') there is no concentration change at the limit of the solution (distance l from the electrode surface), that is, the linear expansion of the system is large enough, the further increase in geometric dimensions does not cause noticeable change.

This condition is usually satisfied [5] if $i > (i'D)^{1/2}$

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(This exists in the cell we use.[2])

Equation (8) expresses the fact that there is no mass flow through the electrode surface.

The Nernst-Peters equation (9) is valid for the reversible electrode reaction. We considered the activity coefficient quotient as unity.

From (9) considering (6) and (2):

$$x = 0, t \geq 0:$$

$$\frac{C_{ox.}}{C_{red.}} = \frac{C_{ox.}^*}{C_{red.}^*} \exp\left(-\frac{nF}{RT} \alpha t\right) = \frac{C_{ox.}^*}{C_{red.}^*} e^{-\alpha t} \quad (9a)$$

where

$$\alpha = \frac{nF}{RT} v$$

Furthermore, the E_1 starting potential is necessarily identical to the system's actual equilibrium redox potential. This agrees with the requirement from (6), that $f(t) = 0$ if $t = 0$.

With the above designation, from (2):

$$E_1 - E = \frac{RT}{nF} \alpha t \quad (10)$$

The solution to the above differential equation system (5) gives the desired $f(t)$ function. [3]

The partial differential equations were converted to ordinary differential equations with the use of the Laplace transformation solved with conditions (7) and (8); and, with the use of the convolution theory, we got the following relationships for $x = 0$ [6,7]:

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$$\begin{aligned} C_{ox.}(0,t) &= C_{ox.}^* - \frac{1}{\sqrt{\pi D_{ox.}}} \int_0^t \frac{f(\tau)}{\sqrt{t-\tau}} d\tau \\ C_{red.}(0,t) &= C_{red.}^* + \frac{1}{\sqrt{\pi D_{red.}}} \int_0^t \frac{f(\tau)}{\sqrt{t-\tau}} d\tau \end{aligned} \quad (11)$$

where τ is the integration variable. (The validity of this mathematical solution is ensured by satisfaction of the boundary conditions.)

From equations (9a) and (11):

$$\int_0^t \frac{f(\tau)}{\sqrt{t-\tau}} d\tau = \frac{C_{ox.}^* \sqrt{\pi D_{ox.}} (1 - e^{-at})}{1 + (C_{ox.}^*/C_{red.}^*) \sqrt{D_{ox.}/D_{red.}}} e^{-at} \quad (12)$$

where $a \geq 0$ (specifically for the cathode reaction $a > 0$).

From the point of view of the dimensions it is advantageous to introduce new variables. If $a > 0$, then

$$\begin{aligned} \tau &= z/a \\ f(\tau) &= C_{ox.}^* \sqrt{\pi D_{ox.}} a \varphi(z) \end{aligned} \quad (13)$$

and thus from (12):

$$\int_0^{at} \frac{\varphi(z)}{\sqrt{at-z}} dz = \frac{1 - e^{-at}}{1 + (C_{ox.}^*/C_{red.}^*) \sqrt{D_{ox.}/D_{red.}}} e^{-at} \quad (14)$$

In the case of $a < 0$, $f(t) < 0$ and thus $i < 0$, so from (12) with the

$$\begin{aligned} \tau &= -z/a \\ f(\tau) &= C_{red.}^* \sqrt{-\pi D_{red.}} a \varphi(z) \end{aligned} \quad (13a)$$

transformation, instead of (14) we get the integral equation:

$$\int_0^{-at} \frac{-\varphi(z)}{\sqrt{-at-z}} dz = \frac{1 - e^{at}}{1 + (C_{red.}^*/C_{ox.}^*) \sqrt{D_{red.}/D_{ox.}}} e^{at} \quad (14a)$$

Thus, during the solution we don't have to deal with the $a < 0$ case separately, we only put $-a$ in place of a , $-\psi$ in place of ψ , and exchange the constants C_{ox}^* and C_{red}^* and D_{ox} and D_{red} .

Numerical Solution

Of the numerous possible solutions to the Abel type integral equation (14) we chose the following:

On the right side of (14) we have a function of at , which we will call $S(at)$. On the left side we partially integrate, considering that ψ in the interval $(0, at)$ has a boundary:

$$2 \int_0^{at} \sqrt{at - z} \varphi'(z) dz = S(at) \quad (15)$$

(ψ' is the derivative according to the argument).

Let's divide the interval $(0, at)$ into δ length equal parts, and write equation (15) in a series for $(0, \delta)$, $(0, 2\delta)$, ..., $(0, n\delta)$ intervals approaching a constant value:

$$\varphi'(z) = \frac{\psi_i - \psi_{i-1}}{\delta}$$

if $(i-1)\delta < z < i\delta$, $i = 1, 2, \dots, n$, where $\psi_1 = \psi(1\delta)$.

Thus we get a linear equation system for evaluating the ψ_n function, which can be progressively calculated:

$$\psi_n = \frac{3}{4\sqrt{\delta}} S(n\delta) - \sum_{i=1}^n [(i+1)^{3/2} - 2i^{3/2} + (i-1)^{3/2}] \psi_{n-i} \quad (16)$$

The calculations were done on the URAL-2 computer with an autocode program at the MTA Computer Technology Center.

We calculated the value of $\sqrt{\delta\pi}(at)$ from zero toward the polarization of the cathode, then the anode, at least a little beyond the place of maximum for (ψ) . The partial interval's δ length is such, that at 25°C for a reaction with 1 electron

RT/nF = 25,6928 mV, according to (10) the potential difference /235 should be 1 millivolt. We gave a variety of values between 0.02 and 1.00 to the parameter $(C_{ox}^* / C_{red}^*) \sqrt{D_{ox} / D_{red}}$ in the S9at) function. (This way we also go the ψ function of the reciprocal of these parameters values, we only had to switch the cathode and anode directions.) In agreement with our expectations and experience, the ψ_n values calculated according to (16) in the case of small values of n contained considerable error, therefore we refined the distribution according to the need. Generally the absolute error of ψ is no larger then 2×10^{-5} .

For verification, we determined the $\psi(at)$ function for the extreme value of $(C_{ox}^* / C_{red}^*) \sqrt{D_{ox} / D_{red}} = 10^6$ as well. We found good agreement with the function determined by Nicholson and Shain [4], which refers to the case when the solution contains only one form of the redox system at the beginning. We compare the maximums of the two functions in Table 1.

Table 1. Maximum of the ψ function when $C_{ox}^* < C_{red}^*$.

	$E^0 - E, \text{ mV}$	$\sqrt{n}\psi$
a)	28,50	0,4463
b)	28,47	0,4463

- a) Data from Nicholson and Shain [4], $C_{red}^* = 0$
 b) Our calculations, $(C_{ox}^* / C_{red}^*) \sqrt{D_{ox} / D_{red}} = 10^6$

Figure 1. shows the progress of the positive branch (ψ_k) of the $\sqrt{\pi^+ \psi}$ function as a function of $E_1 - E$ for a few parameter values (RT/nF = 25.69 mV). Table 2 gives the related maximum data.

We get the current-potential function from the $\psi(at)$ function belonging to the given $(C_{ox}^* / C_{red}^*) \sqrt{D_{ox} / D_{red}}$ value. In the case of cathode polarization ($a > 0$) from (3) and (13):

$$i_k = nFAC_{ox}^* \sqrt{\pi D_{ox} a} \psi_k(at) \quad (17)$$

and in the case of anode polarization ($a < 0$) according the (3) and (13a):

$$i_a = nFAC_{red}^* \sqrt{-\pi D_{red} a} \psi_a(-at) \quad (17a)$$

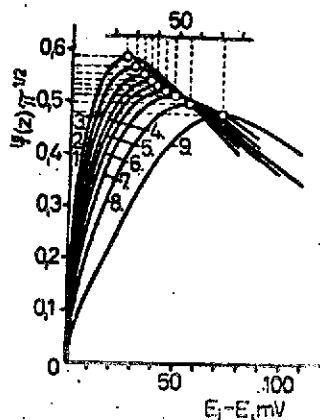


Fig. 1. The progress of the ψ function in the cathode section. (The numbering of the curves refers to the No.--s in Table 2.)

The units in (17) and (17a) are F C/g-eq, A cm², a 1/s, D_{ox} and D_{red} cm²/s, C_{ox}^* and C_{red}^* mole/cm³, and thus we get i_k and i_a in Amp.

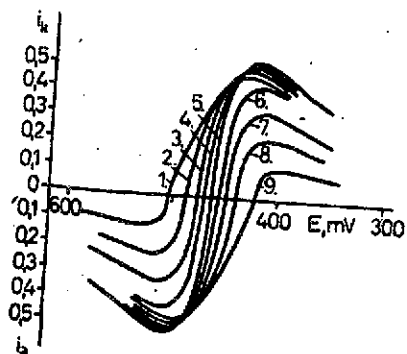
Figure 2 shows the current-potential function (or rather quantities porportional to the current) for the various (hypothetical) C_{ox}^* and C_{red}^* values, assuming that $D_{ox} = D_{red}$ (actually in practice D_{ox} / D_{red} can be considered 1 for most redox systems).

Table 2. Maximum data for the ψ function

Sor- szám	$(C_{ox}^*/C_{red}^*)\sqrt{D_{ox} \cdot D_{red}}$	E_1-E , mV	$\sqrt{\pi} \psi$
1.	0,20	26	0,5840
2.	0,40	30	0,5650
3.	0,60	34	0,5507
4.	0,80	37	0,5396
5.	1,00	40	0,5307
6.	1,25	44	0,5218
7.	1,67	49	0,5107
8.	2,50	56	0,4963
9.	5,00	72	0,4768

Key: 1.) No.

We calculated the E_1 potentials from the redox potential measured at 25°C on a platinum electrode [2] (against a standard hydrogen electrode + 463 mV) in a solution containing 10^{-3} mole/l potassium ferrocyanide, 10^{-3} mole/l potassium ferricyanide and 1 mole/l potassium chloride.



$$D_{ox.} = D_{red.}, nFA/\overline{D(a)} = 1$$

$C_{ox.}^*$	$C_{red.}^*$
1. 0,20	1,00
2. 0,40	1,00
3. 0,60	1,00
4. 0,80	1,00
5. 1,00	1,00
6. 1,00	0,80
7. 1,00	0,60
8. 1,00	0,40
9. 1,00	0,20

Fig. 2. Theoretical current-potential curves for the potassium ferrocyanide - ferricyanide redox system.

If only one from of the redox system is present in the solution, the peak current (i_p) and the peak potential (E_p) can be calculated with the Randles and Sevcik equation [6]:

$$i_p = k_{R.S.} n^{3/2} A C_{ox.}^* \sqrt{D_{ox.} v} \quad (18)$$

$$E_p = E_{1/2} - 1,1 \frac{RT}{nF}$$

for both the cathode and the anode polarization. Here $E_{1/2}$ is the polarographic half-wave potential, $k_{R.S.}$ is a temperature dependent multiplier (at 25°C $k_{R.S.} = 2.69 \times 10^5$) and v is in units V/s. One gets the same result from Nicholson and Shain's calculation.[4]

However, in the presence of both components of the redox system, equations (18) are not entirely accurate, because instead of $k_{R.S.}$

and 1.1 the applied multipliers have to be concentration ratio dependent (connected to the value and place of the ψ function's maximum). Nevertheless, if the concentration ratio is not very different from 1, then the cathode or anode peak current can be considered nearly proportional to the concentration of the oxidized or reduced form, complying with (18). This becomes obvious for example from Fig. 2. In the case of a very large (or very

small] concentration ratio we get the Randles-Sevcik equation's constants from the peak current and peak potential calculated by us, as shown in Table 1.

We deal with further examination of the current-potential curves and their experimental verification in our next paper.

Summary

A theoretical treatment of the reversible voltammetric redox wave at a plane stationary electrode is given. The current-potential function was determined by numerical solution of the semi-infinite linear diffusion problem. The effect of the different concentration ratios of the components of the oxidation-reduction couple was considered. The calculated function corresponds to the Randles-Sevcik equation only at extreme concentration ratios. The results of the calculation allowed to construct the theoretical current-potential curves of the redox waves.

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VOLTAMMETRIC REDOX WAVE AT A STATIONARY ELECTRODE, II
Experimental verification of the current-potential equation.

Tomcsanyi, L., Farsang, G., Rozsonnai, B.

Hungarian Academy of Science Chemical-Structural Research

Laboratory, Budapest

Metallurgy Research Institute, Budapest

In our previous publications we described the technique of /236
cyclical voltammetric redox wave measurement at a stationary
electrode, its analytical application, and the theoretical deri-
vation of its current-potential equation.[1,2]

The theoretical relationships showed that under the circum-
stances of the voltammetric redox wave measurement, i.e. when the
oxidized and reduced forms of the redox system are present in
the solution in concentrations of the same order of magnitude,
the Randles-Sevcik equation is not applicable for the calculation
of the peak current and peak potential.

In the case of a redox wave, the Randles-Sevcik equation's
constants are dependent on the concentration ratio of the oxidized
and reduced forms of the redox system; however, for a given
redox ratio they are independent of the absolute concentrations.
The theoretically derived current-potential equations describe
this phenomenon. [2]

In our experiments we verified the above mentioned theories
for the ferrocyanide-ferricyanide and the ferro- and ferri oxalate
model redox systems at stationary platinum, carbon paste, and
dropping mercury working electrodes, using the previously des-
cribed technique.[1]

Experimental Methods

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Most of our experiments were done with the modified carbon

paste electrode recommended by Adams, [3] We described the preparation of the electrode in our previous publication. [4] The electrode's geometric surface was 0.125 cm^2 . In order to satisfy the condition for one dimensional diffusion, we placed a shading ring at the end of the plexi rod which held the electrode material.

We did measurements with a platinum electrode, which consisted of a 0.16 cm^2 surface platinum plate welded to the end of a glass tube. Before using it we applied the Kublik [5] pretreatment.

We ran a few measurements with the Radiometer company's type P 958b Kemula [6] dropping mercury electrode. The mercury drop had a surface area of 0.017 cm^2 .

We performed the measurements in thermos-like cells shown in Fig. 1 For a reference electrode we used a saturated calomel electrode with a surface area of 3.14 cm^2 , connecting it to the cell through a salt bridge. The salt bridge we always filled with the solution to be measured

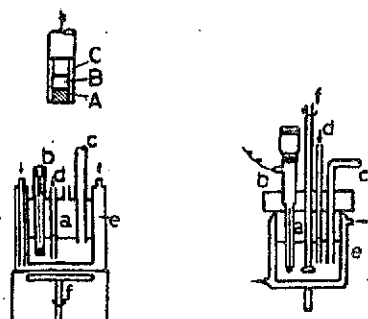


Fig. 1. The arrangement of voltammetric cells: a - electrode dish, b- working electrode c- salt bridge, d- gas inlet tube, e- thermos cape, f- stirrer. A- carbon paste, B- copper block, C- plexi rod.

All measurements were done at $25.0 \pm 0.2^\circ\text{C}$.

For the polarization curves we used the RADELKIS type OH-102 and the Radiometer type PO-4g polarographs.

The solutions used in the experiments were prepared from p.a. grade chemicals. The potassium chloride and sodium oxalate used for the base electrolyte

Experimental Results

Equations Relating to the Peak current

According to our earlier theoretical derivation [2], the following equations are valid for the peak current of a voltammetric redox wave at a stationary electrode in a base electrolyte containing both forms of the reversible redox system in concentrations of the same order of magnitude.

$$i_{p.k.} = nFAC_{ox}\sqrt{\pi D_{ox}a} \psi_k(at)_{max.} \quad (1)$$

$$i_{p.a.} = nFAC_{red}\sqrt{-\pi D_{red}a} \psi_a(-at)_{max.} \quad (2)$$

where $i_{p.k.}$ and $i_{p.a.}$ are the cathode and anode peak currents in Amp., n is the electron number change in the electrode reaction, F is the Faraday number, A is the electrode surface area in cm^2 , C_{ox} and C_{red} are the concentrations of the oxidized and reduced forms of the redox system, D_{ox} and D_{red} are the diffusion constants of the oxidized and reduced forms of the redox system;

$$a = \frac{RTv}{nF}$$

where v is the speed of polarization in V/s, R is the universal gas constant, T is the absolute temperature; $\psi_k(at)_{max.}$ and $\psi_a(at)_{max.}$ are the maximum values of the function expressing the time and potential dependent change in the surface concentration gradient.

The two derived equations differ from the Randles-Sevcik equation in the maximum value of the function which expresses the time and potential dependent change in the surface concentration gradient. In the case of redox waves, as we demonstrated in our previous article [2], the maximum value only approaches the value found in the Randles-Sevcik equation in limiting instances (very large or very small oxidized-reduced concentration ratio). Although the maximum value of the redox wave's $\psi(at)$

function for a given redox ratio does not depend on the absolute concentration of the participating component, it is a function of the concentration ratio of the oxidized and reduced forms of the redox system. When the concentrations of the oxidized and reduced form are the same order of magnitude, within the redox ratio interval of 0.2 - 5.0, theoretically the maximum value of the function changes $\pm 10\%$ (basing it on the value of the function for a redox ratio of 1) [2].

In the ferrous-ferric cyanide redox system with platinum or carbon paste electrodes the maximum value of the $\psi(at)$ function calculated from experimental data is in good agreement with the theoretical value. The calculated and the measured values are shown in Table 1. The calculations were performed according to equations (1) and (2), using the geometrical electrode surface and diffusion constants measured by Stackelberg et. al. [7] under identical circumstances.

As shown in Table 1, values calculated from data obtained from measurements with a platinum electrode are in good agreement with theoretical values, while measurements with the carbon paste electrode give smaller values. In both cases the change of the maximum value of the $\psi(at)$ function agrees with the theoretical value changes.

The probable reason for the deviation in the values obtained with the carbon paste electrode is that the calculations were performed using the geometrical electrode surface. However, the electrochemically active electrode surface nearly always differs from the geometrical electrode surface, and is usually larger. In voltammetric measurements according to Delahay [8], in the neighborhood of the peak current the electrochemically active surface may be considered identical to the geometrical surface, due to the decrease in the number of so called "gaps". According

to the data in Table 1, this is true for the platinum electrode. However, for the carbon paste electrode, where the surface is hydrophobic due to the characteristics of the carbon and the paste-forming liquid, wetting problems arise, and thus we assume that the effective surface is smaller than that calculated from the geometrical data.

Table 1. The change in the values of $\psi(at)_{max}$ as a function of the redox ratio, in a 10^{-3} mole/l KCL base solution containing 10^{-3} - 10^{-4} mole/l ferrocyanide and ferricyanide at a stationary platinum and carbon paste electrode. /238

$$A_{Pt} = 0,16 \text{ cm}^2; A_{Cp} = 0,125 \text{ cm}^2; D_{ox.} = 7,6 \cdot 10^{-6} \\ D_{red.} = 6,3 \cdot 10^{-6} \text{ cm}^2/\text{s}; v = 0,025 \text{ V/s}.$$

$C_{red.}$	$\frac{C_{ox.}}{C_{red.}}$	$\psi_a(at)_{max}$ értékeinek változása		
		2 elméleti	3 platina- elektro- don mérve	4 szén- paszta- elektro- don mérve
$[\text{Fe}(\text{CN})_6^{4-}] = 1 \cdot 10^{-3}$ mól/l	0,2	0,330	0,365	0,236
	0,4	0,319	0,324	0,202
	0,6	0,311	0,321	0,198
	0,8	0,305	0,289	0,195
	1,0	0,300	0,290	0,180
	1,25	0,293	0,283	0,180
	1,67	0,288	0,298	0,181
	2,5	0,280	0,278	0,181
	5,0	0,269	0,256	0,189
	0,2	0,269	0,249	0,172
$[\text{Fe}(\text{CN})_6^{4-}] = 1 \cdot 10^{-4}$ mól/l	0,4	0,280	0,249	0,172
	0,6	0,288	0,253	0,172
	0,8	0,293	0,264	0,174
	1,0	0,300	0,276	0,175
	1,25	0,305	0,280	0,177
	1,67	0,311	0,292	0,178
	2,5	0,319	0,315	0,189
	5,0	0,330	0,300	0,215

Key: 1. change in $\psi(at)_{max}$ values
2. theoretical
3. measured at platinum electrode
4. measured at carbon paste electrode

We examined the ferro- ferri oxalate system using a dropping mercury working electrode. In this case, due to the spherical

shape of the electrode the sphere-symmetrical diffusion equations apply, and the experimentally measured data only approximate the theoretical values of the $\psi(at)$ function. According to Berzins and Delahay [9], one can apply the peak current relationships for one dimensional diffusion in the case of sphere-symmetrical diffusion as well, if the following condition is met:

$$\frac{D\tau}{r^2} \leq 3 \cdot 10^{-3} \quad (3)$$

where τ is the transition time and r is the radius of the sphere electrode. If this condition is satisfied, the difference between the equations derived for planar and sphere-symmetrical diffusion is within 5%. During our measurements, condition (3) was not satisfied (the expression on the left gave a value of 10^{-2}) and therefore the deviation from the calculated value was more than 5%. For the above reason we calculated the maximum value of the $\psi(at)$ function only for the case of identical concentration of the oxidized and reduced forms. The calculations were performed according to equations (1) and (2), using geometrical electrode surface and the polarographically determined diffusion coefficient. The results are shown in Table 2.

Table 2. Value of $\psi(at)_{\max}$ at a dropping mercury electrode, in a 1% H_2SO_4 base solution containing 0.2 mole/l sodium oxalate and 10^{-3} mole/l ferro- and ferri oxalate.

$$A = 0,017 \text{ cm}^2; D_{ox.} = 7,1 \cdot 10^{-6} \text{ cm}^2/\text{s}; \\ D_{red.} = 5,8 \cdot 10^{-6} \text{ cm}^2/\text{s}; \quad v = 0,0066 \text{ V/s}$$

	$\psi_s(at)_{\max}$	$\psi_K(at)_{\max}$
Elméleti érték 1.)	0,300	0,300
Mért érték 2.)	0,290	0,304

Key: 1. Theoretical value
2. Measured value

The main purpose of the experiments with the dropping mercury electrode was to evaluate the effect of the speed of polarization.

Table 3 contains the results of the measurements, from which the peak current-polarization speed functions were calculated, as shown in Figure 2.

Table 3. The examination of ferro- and ferri oxalate redox system with dropping mercury electrode in a 1% H₂SO₄ base solution containing 0.2 mole/l sodium oxalate, with various polarization speeds.

Koncentráció, mol/l 1)	Polarizáció sebesség, V/min 2)	i_{pa} μA	i_{pk} μA
a) $C_{ox.} = 2 \cdot 10^{-4}$ $C_{red.} = 8 \cdot 10^{-4}$	0,1	0,488	0,136
	0,2	0,624	0,180
	0,4	0,824	0,264
	0,8	1,10	0,348
b) $C_{ox.} = 1 \cdot 10^{-3}$ $C_{red.} = 1 \cdot 10^{-3}$	0,1	0,600	0,760
	0,2	0,748	0,980
	0,4	1,03	1,28
	0,8	1,36	1,68
c) $C_{ox.} = 9 \cdot 10^{-4}$ $C_{red.} = 1 \cdot 10^{-4}$	0,1	0,064	0,560
	0,2	0,088	0,744
	0,4	0,108	0,960
	0,8	0,156	1,28

Key: 1. Concentration, mole/l
2. Polarization speed, V/min

The anode and the cathode peak current values of all redox ratios shown in Fig. 2 are directly proportional to square root of the polarization speed, thus the square root relationship shown in equations (1) and (2) is valid. Thus, with respect to the change in polarization speed, the redox wave behaves identically to the cyclical voltammetric curves of a solution containing only one component of the redox system.

Equations Relating to the Peak Potential

In a base electrolyte containing both forms of a reversible redox system, the following equations are valid for the peak potential of the voltammetric redox wave at a stationary electrode:

$$E_{pk} = E_k - K_k \frac{RT}{nF} \quad (4) \quad \frac{239}{7}$$

$$E_{p.a.} = E_1 + K_a \frac{RT}{nF}$$

(5)

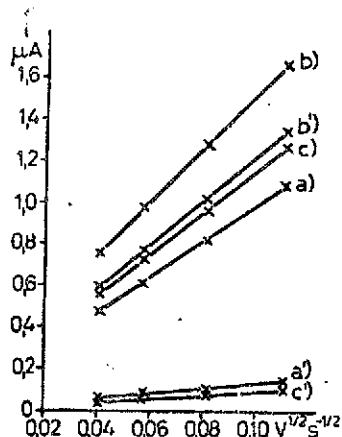


Fig. 2. The formation of the peak current-polarization speed function of redox waves at a dropping mercury electrode in a base solution of 1% H_2SO_4 containing ferro- and ferri oxalate. The a), b), c), curves represent the cathode peak current functions similarly marked in Table 3, and a'), b'), c') curves refer to the anode.

where $E_{p.k.}$ and $E_{p.a.}$ are the cathode and anode peak potentials, K_k and K_a are the maximum points of the $\psi(at)$ function.

Our equation appears similar to the Randles-Sevcik equation. However, while for voltammetric curves of a solution containing only one component of the redox system the value of K is constant, in the case of the redox wave it changes depending on the concentration ratio of the oxidized and reduced forms.

In table 4 we show the change of the peak potential, (the value of RT/nF), as a function of the redox ratio, for the ferro- ferri-cyanide redox system at a stationary platinum electrode.

The distortion due to the inertia of the compensograph could not be eliminated, and this caused the small deviations in the measurements with the platinum electrode.

The direction of the change in the peak potential values in the same as the direction of the theoretical change.

Theoretical and Measured Current-Potential curves

With the knowledge of the equations for the peak current and peak potential, we examined the theoretical and experimental current-potential curves. The current-potential curves measured

Table 4. Changes in the $E_p - E_1$ values as a function of the redox ratio in a base solution of 1 mole/l potassium chloride containing 10^{-3} - 10^{-4} mole/l ferro-cyanide and ferri-cyanide at a stationary platinum electrode ($v = 1.5$ V/min)

C_{red}	$\frac{C_{ox}}{C_{red}}$	1 $E_{p.a.} - E_1$ értékek változása, V	
		2 elméleti	3 platina-elektrodon mérve
$[Fe(CN)_6^{4-}] = 1 \cdot 10^{-3}$ mól/l	0,2	0,03	0,06
	0,4	0,03	0,07
	0,6	0,03	0,07
	0,8	0,04	0,08
	1,0	0,04	0,09
	1,25	0,04	0,09
	1,67	0,05	0,09
	2,5	0,06	0,11
	5,0	0,07	0,11
	0,2	0,07	0,10
$[Fe(CN)_6^{4-}] = 1 \cdot 10^{-4}$ mól/l	0,4	0,06	0,09
	0,6	0,05	0,09
	0,8	0,04	0,09
	1,0	0,04	0,09
	1,25	0,04	0,09
	1,67	0,03	0,08
	2,5	0,03	0,07
	5,0	0,03	0,06
	0,2	0,07	0,10
	0,4	0,06	0,09

Key: 1. Change in the $E_{p.a.} - E_1$ value, V
 2. Theoretical
 3. Measured with platinum electrode

with a carbon paste electrode showed greater deviation from the theoretical curves, due to the quasi-reversible behavior of the ferro- and ferri-cyanide system with this electrode, as well as the difference between the effective and geometrical electrode surface.

Figure 3 shows the theoretically calculated redox waves and those measured with a platinum and a dropping mercury electrode.

The reason for the deviation of the curves measured with a platinum electrode from the theoretical redox waves, is the inertia of the current registering instrument. In the case of the redox waves measured with a dropping mercury electrode,

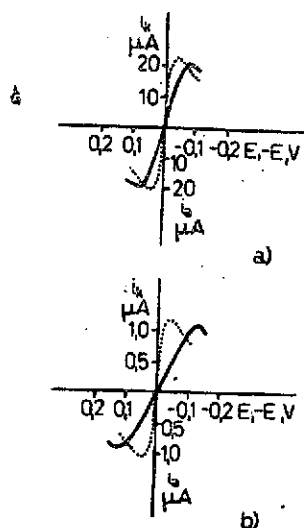


Fig. 3. Theoretical and experimentally obtained redox waves: a) redox wave measured with a platinum electrode in a base solution of 1 mole/l KCl containing 1×10^{-3} mole/l potassium ferro-cyanide and potassium ferri-cyanide; b) redox wave measured with a dropping mercury electrode in a base solution of 0.2 mole/l sodium oxalate in 1% H_2SO_4 , containing 1×10^{-3} mole/l ferro- and ferri oxalate.

----- theoretical current-potential curves

———— measured current-potential curves.

current-concentration function. It must be considered that the accuracy of the cyclical voltammetric measurements during routine analytical experiments is no better than a few %. In practice, due to the presence of the oxidized and reduced forms in concentrations of the same order of magnitude, the redox ratio usually does not change beyond the 0.2-5.0 interval, and thus

additional error is caused by the difference between the planar and sphere-symmetrical surface diffusion, which we did not consider in our calculations.

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Analytical Application of the Cyclical Voltammetric Redox Wave

The criteria of the analytical applicability of the redox wave are, that the measured data - in this case the peak current values - should be reproducible, and there should be a direct correlation between the concentration and the peak current values.

As can be seen from the peak current equations - equations (1) and (2) - in the first approach the peak current value is directly proportional to the deplorizer concentration. The change of the maximum value of the $\psi(at)$ function relative to the redox ratio creates the non-linear peak

a small deviation from the linear does not cause significant error in measurement.

If greater precision is required, or there is a greater change in the redox ratio, the use of a calibration curve is recommended for the evaluation of the measurements. With the use of the calibration curve the accuracy of the method according to the reproducibility of the voltammetric curve is 1-2%.

Summary

Equations derived for the voltammetric redox wave were verified experimentally at stationary platinum, carbon paste and dropping mercury electrodes. The ferrous-ferric-cyanide and ferrous-ferric oxalate redox systems were investigated. The peak currents and peak potentials of the redox waves are in exact agreement with the theoretical results only for the stationary platinum electrode. The quasi-reversible electron transfer process gave rise to greater differences with carbon paste electrode, and the sphericity of the electrode caused some slight differences in the case of a dropping mercury electrode.

It was possible to determine the limitations and the exact conditions for the analytical application of the redox wave by comparison of the experimental results and theoretical calculations.

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